LIP Characteristics of Nanostructured ZnO Thin Films

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***Abstract*- In this study, we investigate the dependence of laser induced plasma spectroscopy LIPS plasma characteristics on the nanostructured and bulk ZnO targets. This study was performed using 670 mJ of the fundamental wavelength of Nd:YAG laser energy and 5 ns pulse width focused normal to the surface of the sample. The analysis of the observed emission spectra revealed the zinc characteristic spectral lines with high resolution for both samples. It is found that the plasma electron temperature reaches values of 4131 ±5% Kelvin for bulk and 5107 ±5% Kelvin for nano - ZnO samples. Furthermore, the average values of electron density Ne (bulk) found to be 8.47E+15 cm^{-3} while Ne(nano) reaches 1.24E+16 cm^{-3}. These results indicate that both plasma temperature and electron density are increased in case of nanostructured ZnO more than the bulk case. This is due to changing the martial matrix, which affect the plasma profile.**

Keywords- ZnO, Plasma density, LIPS spectroscopy, nanostrcuture.

I. INTRODUCTION

Over the past three decades, Laser-induced plasma spectroscopy (LIPS) or laser spark spectroscopy (LSS) has developed rapidly as an analytical technique [1]. LIPS can be applied for analysis of solids, liquids, and gases without further complicated preparation procedures or especial environmental conditions. LIPS employs a pulsed laser-generated plasma as the hot vaporization, atomization and excitation source. LIPS is a rather direct plasma spectra technology, employing high flux laser pulses (~ 10^9 W/cm2) to irradiate a sample, thereby producing plasma with a small amount of ablated material. A portion of the plasma light is collected via a fiber optic cable and a spectrometer disperses the light emitted by ionic and excited atomic species in the plasma, a detector records the emission signals, and fast electronics take over to digitize these signals and display the results. ZnO thin film represents one of the most attractive inexpensive oxide thin films with a wide band gap semiconductor, and has useful applications in the field of optoelectronic devices such as ultraviolet light emitting diodes, blue luminescent devices, solar cells & photo catalysts [2]. On the other hand, behavior of light interaction with bulk materials also changes drastically as we go down to the nano size of the materials. This is due to decrease in the dimensions below the critical wavelength of light [3].

In this work, a comparison of plasma characteristic is studied for both bulk and nano - ZnO materials using LIPS technique. Both electron temperature and electron density are determined for the two kind of ZnO structures.

II. EXPERIMENTAL PROCEDURE

A. Samples

The ZnO nano samples was purchased from commercial company (M K Impex Corp. Canada) [4]. The purification of these samples was 99.9% with average particle size of 20 nm for nano powder ZnO samples. To facilitate a uniform interaction area with the laser, the nano samples were prepared as disk shaped tablets. ZnO discs were prepared via the conventional ceramic processing method involving ball milling, drying, pressing (5 tons/cm^2.) and sintering (1200°C).

B. The LIPS system

A Q-Switched Nd: YAG laser (Brilliant-B , Quantel) operating at its fundamental harmonic (1064 nm) and pulse duration of 5 ns at FWHM with a repetition rate of 10 Hz It has also the ability to focus on a fresh region of the sample through a short focal length for each successive pulse. In this experiment,

This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

978-1-4799-2569-8/13/$31.00 ©2013 IEEE

the laser fluence kept fixed at a level of 387 J/cm^2 using a lens of 9 cm focal length. The schematic diagram of the used LIPS setup is similar to the standard LIPS shown before elsewhere [5]. Briefly, Spectroscopic system consists of SE200 Echelle spectrograph (Catalina, model SE 200) and ICCD camera (Andor, model iStar DH734-18F) that covers the range 190 - 1100 nm of wavelength for optical signals after 1μs gate delay and 1μs gate width (the ICCD collection time). The laser radiation was focused by the 9 cm convex lens onto the ZnO target to ablate material from the sample surface and produce a plasma cloud. A bundle of optical fiber of 600 μm diameter was used to collect the radiation emitted by the generated plasma cloud. This collected light was then delivered to a high-resolution (0.1 nm FWHM) spectrometer attached to a gated CCD. For each LIBS spectrum, an average of 10 collected spectra was recorded for the completely active range from 190 – 1100 nm.

III. RESULTS AND DISCUSSION

Figure 1 (A,B) show typical LIPS spectra for Zinc oxide Bulk and nano-structured films simultaneously using an Echelle Spectrometer over 200-1000 nm range of wavelengths. The enhancement in LIPS signal is clearly shown in fig.1B for the wavelength range 328-336 nm. The later figure clearly revealed an intensity enhancement in the observed spectral lines intensities in case of nano compare to bulk ZnO samples.A complete list of the observed zinc spectral lines is listed in table 1 with their corresponding spectroscopic data.

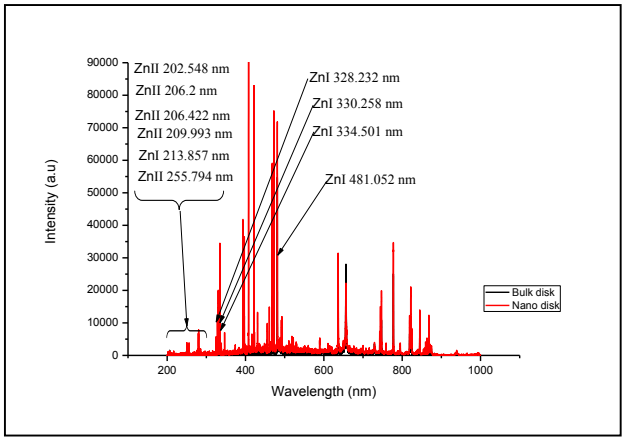

Fig. (1) A : LIPS signal of bulky Zn sample (black line) and nano–structured film of Zn (red line) for the whole wavelength range 200 – 1000 nm.

The excitation state intensity of emitted spectra line can be used to calculate the plasma temperature using the well-known Boltzmann eq. [6] as:

$$\ln\frac{I\lambda}{A_{ki}g_k} = -\frac{1}{KT}.E_k + \ln\frac{C\cdot F}{U(T)} \qquad (1)$$

where λ is the wave length, A_{ki} is the transition probability, g_k is the statistical weight for the upper level, E_k is the excited

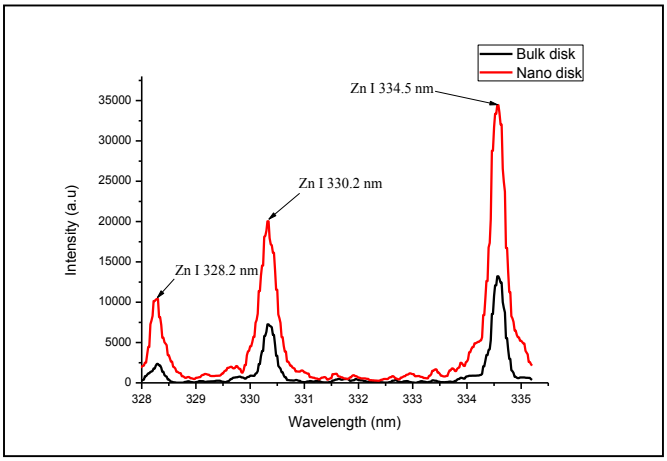

Fig. (1) B : LIPS signal of bulky Zn sample (black line) and nano–structured film of Zn (red line) for the wavelength range of interest 328-336 nm.

level energy, T is the plasma temperature (Kelvin) , K is the Boltzmann constants, U(T) is the partition function, F is an experimental factor and C is the species concentration.

Table 1 Resolved spectral lines in a time-integrated spectrum of ZnO sample.

λ (nm)	$(A_{ki})(g_k)$ (s^{-1})	E_k (cm^{-1})
202.548	1.30E+09	49355.03
206.2	1.30E+09	48481
206.422	1.80E+09	96909.74
209.993	3.40E+09	96960.39
213.857	2.13E+09	46745.41
255.794	2.13E+09	88437.14
328.232	2.70E+08	62768.75
330.258	6.00E+08	62772.02
334.501	1.20E+09	62776.99
481.052	1.40E+07	53672.28

By applying (1) for Zn excitation energies transitions 49355.03, 46745.41, 62768.75, 62772.02, 46745.41 cm^{-1} , using their corresponding spectroscopic data (from table 1) [8], it is found that the electron temperature reaches values of 4131 ±5% K for bulk and 5107 ±5% K for nano- ZnO samples as shown in fig.2.

Several authors [5,6] confirmed that using the Stark broadening of a well isolated spectral line and the FWHM of that line the electron density (in cm^{-3}) could be determined from the formula ;

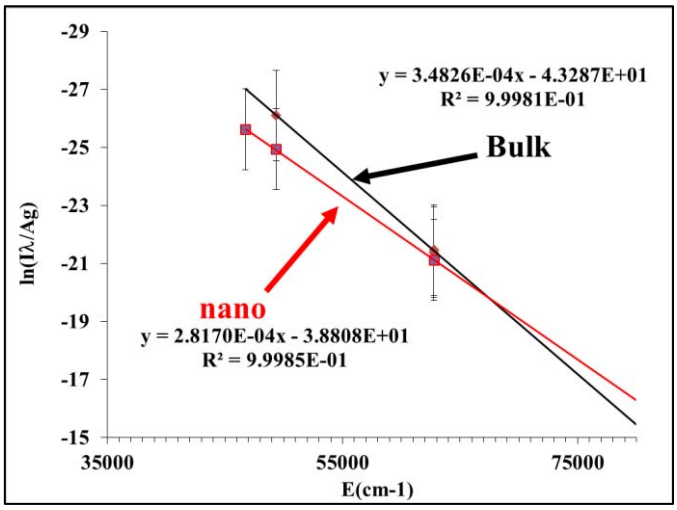

Fig. 2 Boltz. plots of ln (Iλ/Ag) versus E for bulk & nano ZnO samples.

$$N_e \approx \left(\frac{\Delta\lambda_{FWHM}}{2.w} \right).10^{16} \qquad (2)$$

w is the electron impact parameter (stark broadening value). The last formula is generally used for calculations of plasma generated from solid targets [7].

The electron density is determined by measuring the broadening (FWHM) of a suitable emission line of the laser-plasma spectrum. Figures 3 (A-C) show Lorentzian curve fitting to determine the values of ($\lambda_{1/2}$) for 328.067 nm, 334.501 nm, and 481.052 nm for both the bulk and nano samples, respectively. By substituting of the stark broadening values [from ref. 7] and ($\lambda_{1/2}$) values at table 2, in eq. (2) above, the plasma electron density Ne is determined for both bulk and nano structure ZnO samples. It is found that Ne(average) (bulk) = 8.47E+15 cm^{-3} while Ne (average) (nano) = 1.24E+16 cm^{-3}.

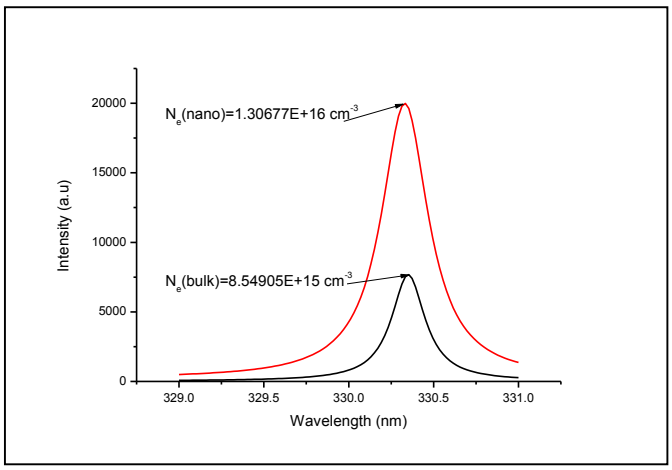

Fig. 3A Lorentzian curve fitting for Zn 330.258 nm for the bulk and nano ZnO samples.

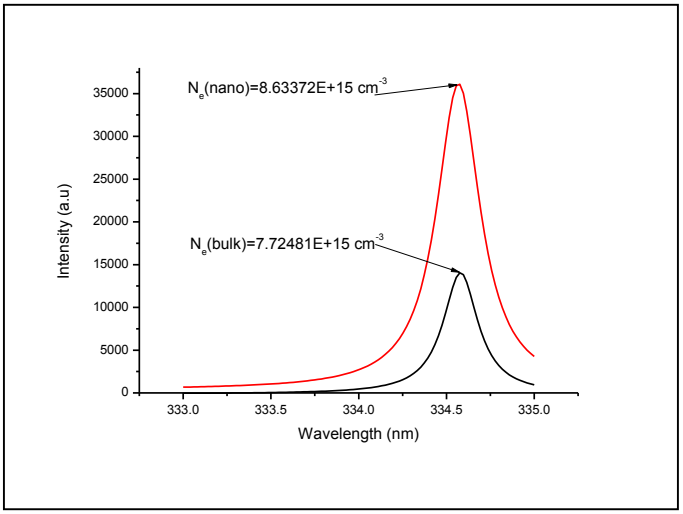

Fig. 3B Lorentzian curve fitting for Zn 334.501nm for the ZnO bulk and nano samples.

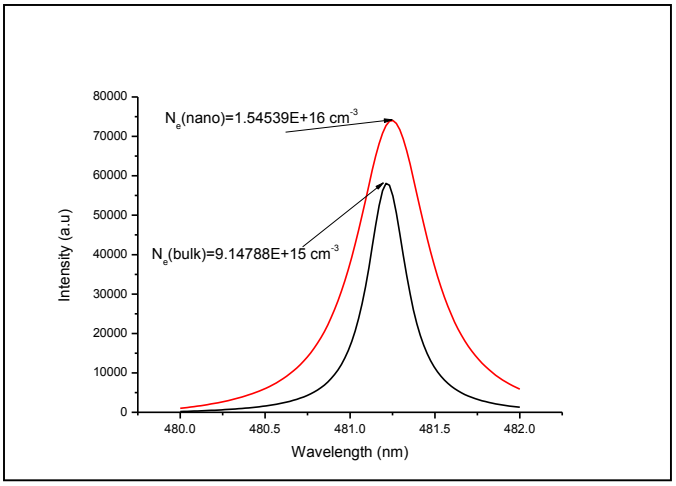

Fig. 3C Lorentzian curve fitting for Zn 481.052 nm for the bulk and nano ZnO samples.

The above observed results indicate that both electron density and temperature increased in case of nanostructured than bulk ZnO. These results indicate that behavior of light interaction with materials also changes drastically as we go down to the nano grain size of the materials. A similar behavior observed before for nano-gold-particles due to decrease in the dimensions below the critical wavelength of light [3]. It's worth noting that, in the nano scale materials, interaction on atomic scale dominates and exhibits quantum mechanical behavior as compared to bulk materials [3]. In macroscopic scale, changing the sample matrix affect the light interaction with matter as found before for other matrices [7].

Table2. A list of the measured line widths ($\lambda_{1/2}$) and the stark broadening (w) values for Zn at 328.067 nm, 334.501 nm, and 481.052 nm the corresponding plasma density values of bulk and nano ZnO samples.

λ (nm)	2W (nm)	$\Delta\lambda_1$ (nm)	Ne (cm^{-3})
330.25	2.80E-01	(bulk) 0.23901 (nano) 0.33671	(bulk) 8.54905E+15 (nano) 1.30677E+16
334.50	3.48E-01	(bulk) 0.26045 (nano) 0.30878	(bulk) 7.72481E+15 (nano) 8.63372E+15
481.05	3.30E-01	(bulk) 0.28264 (nano) 0.51708	(bulk) 9.14788E+15 (nano) 1.54539E+16

IV Conclusion

In this study by using LIPS technique, it is found that the plasma characterizations of ZnO nanostructured thin films are different from bulk structure case using a fixed laser fluence on the sample. This study is important for many industrial application purposes.

ACKNOWLEDGMENT

This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

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